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COMPLETE SPECIFICATION

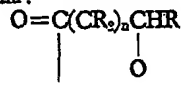
Isocyanate-extended Polyoxyalkylene-Carboxy-Alkylene Polymers

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (assignee of DONALD MACKEY YOUNG and FRITZ HOSTETTLER), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

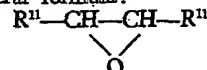
The present invention relates to synthetic compositions of matter useful in the manufacture of tires, shoe soles, belts and many other articles desirably having high resistance to abrasion, oxidation, solvents and ultra-violet light, as well as to a method of preparing such compositions.

We have also found that polyurethane resins can advantageously be prepared from oxyalkylene-carboxyalkylene polymers in which the oxy and carboxy groups, or oxyalkylene and carboxyalkylene links, are distributed in random or ordered fashion along the lengths of the chains and that these can be prepared essentially by reaction of a lactone with an epoxide and a difunctional focal compound preferably in the presence of a catalyst.

According to the present invention there is provided a method of preparing a gum stock which comprises forming a mixture of oxyalkylene-carboxyalkylene polymers by reacting a diphenol, a diol, a diamine, an amino alcohol, a dimercaptan, a mercapto alcohol, water or hydrogen sulphide, a lactone of the general formula:—



in which n is an integer having a value of at least 2, all the R s are hydrogen, when n is 2, at least 6 R s are hydrogen when n is more than 2 and the remaining R s are hydrogen or alkyl, cycloalkyl, alkoxy or single ring aromatic hydrocarbon radicals or an hydroxy ester of said lactone and a primary or secondary alcohol having a boiling point lower than that of said diol, diamine, amino alcohol, dimercaptan, mercapto alcohol, water, hydrogen sulphide or diphenol, and a 1, 2 epoxide of the general formula:—



in which R'' is hydrogen or an alkyl, chloroalkyl, hydroxyalkyl, vinyl or phenyl radical or in which the two R'' s taken together complete a closed hydrocarbon ring; reacting said reaction mixture with a molar excess as hereinbefore defined of an organic diisocyanate to form isocyanate-extended oxyalkylene-carboxyalkylene polymers and converting said polymers to a non-hardening gum stock by reaction with a diol, a diamine or an amino alcohol.

The polyurethane resins of the present invention are characterized by the presence of substantially linear units of conjugated oxyalkylene-carboxyalkylene chains and diisocyanate residues in which the chains and residues are connected to one another by means of urethane groups and the chains comprise substantially linear series of interconnected divalent oxyalkylene and monocarboxyalkylene links. In the chains of these resins the connecting oxy and carboxy groups between the alkylene segments are distributed in ordered or random fashion. Thus, for example, a typical chain with ordered distribution may be represented by:—

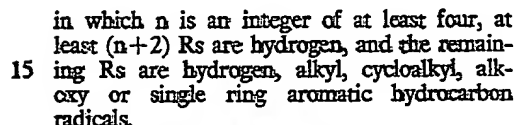
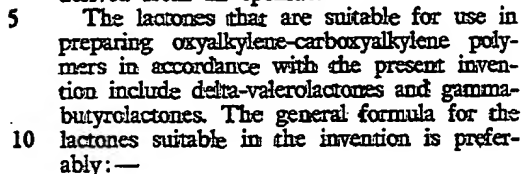


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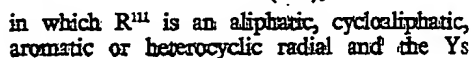
in which the Es stand for alkylene segments derived from an epoxide.



VI.

$$\begin{array}{c} \text{R}^{11} \quad \text{R}^{11} \\ | \quad | \\ \text{CH} - \text{CH} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$$

40 The difunctional focal compounds, so-called because they act as focal points in the formation of oxyalkylene-carboxyalkylene polymers and play a major role in determining the molecular weight of a given mixture
45 of oxyalkylene-carboxyalkylene polymers, are those having two reactive hydrogens that are capable of opening a lactone ring or an epoxide. The difunctional compounds useful as such are diols, diamines, diphenols, dimercaptans, amino alcohols and mercapto alcohols represented by the formula:—
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alcohols such as aliphatic amino alcohols of the general formula $\text{HO}(\text{CH}_2)_n\text{NH}_2$, where n equals two to ten, N-methylethanolamine, isopropanolamine, N-methylisopropanolamine; aromatic amino alcohols such as para-amino-phenethyl alcohol and para-amino-alpha-methylbenzyl alcohol; various cycloaliphatic amino alcohols such as 4-aminocyclohexanol; diamines of the general formula $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$, monosecondary diamines of the general formula $\text{R}^{\text{III}}\text{NH}(\text{CH}_2)_n\text{NH}_2$, and dissecondary diamines of the general formula $\text{R}^{\text{III}}\text{NH}(\text{CH}_2)_n\text{NHR}^{\text{III}}$, where n equals two to ten and where R^{III} is alkyl, aryl, aralkyl or cycloalkyl; aromatic diamines such as meta-phenylenediamine, paraphenylenediamine, toluene-2,4-diamine, toluene-2,6-diamine, 1,5-naphthalenediamine, 1,8 - naphthalenediamine, meta-xilylenediamine, para-xilylenediamine, benzidine, 3,3'-dimethyl-4,4'-biphenyldiamine, 3,3'-dimethoxy-4,4'-biphenyldiamine, 3,3'-di-

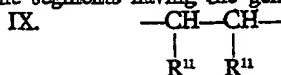
The oxyalkylene-carboxyalkylene polymers

prepared from these starting materials in accordance with the present invention are

believed to correspond predominantly to the general formula:—



in which the Ys and R^{III} are as defined earlier, and the Ls are substantially linear lactone residues or alkylene segments having the general formula $-(\text{CR}_2)_n\text{CHR}-$ in which n and the Rs are as described with reference to Formula V, the Es are alkylene segments having the general formula:—

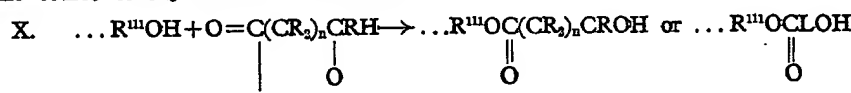


wherein the R^{II}s are as described with reference to Formula VI, the ms are an average of at least one, the xs average from about one-half to about six and one-half, the ys average from about one to about fifty, and the Ls and Es are in random or ordered distribution, at least some of the Ls in a given series being recurrent, i.e., separated from one another by Es, or at least some the Es in a given series being recurrent, i.e., separated from one another by Ls.

While we do not wish to be limited by any theory presented herein, it is believed that the lactone and epoxide molecules are opened in the course of the reaction to form sub-

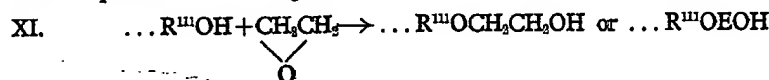
stantially linear carboxyalkylene and oxyalkylene links, respectively, i.e. substituted or unsubstituted alkylene segments having terminal carboxy and oxy groups. The opening of one such lactone or epoxide molecule produces a chain link having a terminal hydroxyl group which can then open another lactone or epoxide molecule. This produces a lengthening of the chain and the formation of still another hydroxyl for again opening a lactone ring or epoxide bridge. Additional lactone and epoxide residues add on in random or ordered fashion to form a chain of recurrent lactone residues and epoxide residues, said chain in essence comprising a series of alkylene links connected to another by divalent carboxy groups and oxy groups.

To illustrate, it is believed that a lactone is opened by reaction with a hydroxyl group and thus converted into an alkylene segment connected by a carboxy group at one end to a diol residue, for example, and by an oxy group at the other end to a terminal hydrogen, thus:—



If more lactone molecules are available, they will form and add to previous links in the same manner. Epoxides are also opened

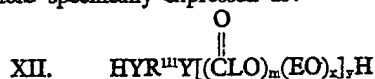
by hydroxyl groups to form ethylene segments. Thus, for example, ethylene oxide will react with a terminal OH group:—



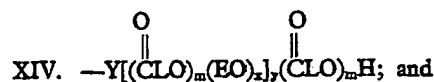
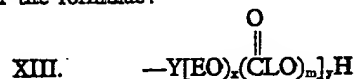
If more epoxide molecules are available, they will add to previous groups in the same manner, forming polyoxyethylene chains. When a lactone and an epoxide are both available, they are believed to react in essentially the same manner and add in random fashion to form polyoxyalkylene chains interrupted occasionally by carboxy groups.

It is to be understood and emphasized, therefore, that the Ls and Es in Formula VIII, for example, can be in random ordered distribution and that the formula represents the predominant structure of the oxyalkylene-carboxyalkylene polymers. The values of m and x in the individual $(\text{CLO})_m(\text{EO})_x$ chain

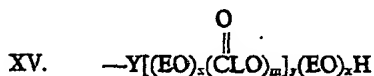
same. The y of one chain may in fact equal zero, in which instance the formula may be more specifically expressed as:—



The distribution of the L and E groups in the oxyalkylene-carboxyalkylene polymers is such that a lactone residue may occur at either or both ends of a chain and an epoxide residue may like wise occur at either or both ends of a series. The general formula is therefore intended to include structures that may more specifically be set forth as having chains of the formulae:—



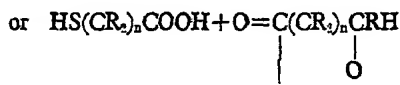
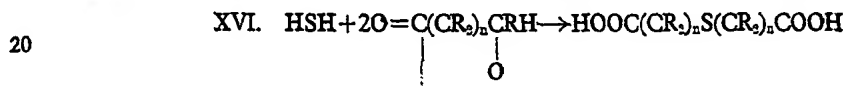
portions may be the same or different and the lengths and structures of the various $-\text{Y}[(\text{CLO})_m(\text{EO})_x]_z \text{H}$ chains need not be the



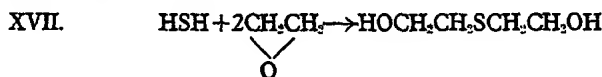
It will also be apparent that there are at least three methylene groups in any opened lactone residue symbolized by L in the formulae and further identified as adjoining at least one carbonyl group of a connecting carboxy group. The opened epoxide residues symbolized in the formulae by E and further

identified as positioned between oxy groups, some of which may be connected to carbonyl groups to form carboxy links, contain two methylene groups. Where substituted lactones and substituted 1,2-epoxides are used, the alkylene segments of the respective opened residues will be correspondingly substituted.

When water is used in place of organic polyfunctional compounds, the reactions are essentially the same. With hydrogen sulfide, lactones are believed to add on:—



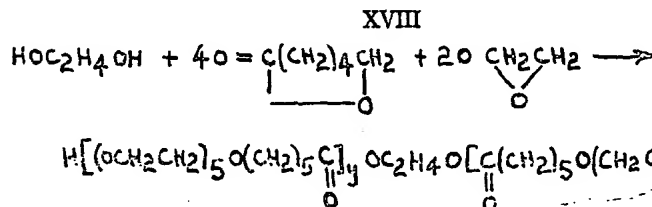
and epoxides would open and add:—



Additional lactones and epoxides would be opened and add to the chains in the manner described.

A preferred and most direct method of preparing the oxyalkylene-carboxyalkylene polymers in the first stage, provided the difunctional focal compounds chosen do not contain nitrogen atoms carrying reactive hydrogen atoms, is to react the three initial

materials described, i.e., the lactone, the epoxide and the difunctional compound, at an elevated temperature in the presence of a catalyst. By way of illustration, the reaction of ethylene glycol, unsubstituted epsilon-caprolactone and ethylene oxide in accordance with this embodiment of the invention may, for example, be represented by the equation:—



the ethylene and pentamethylene segments, and therefore also the oxy and carboxy groups, however being distributed in random fashion within the brackets and the ys being an average of two.

The distribution of the lactone and epoxide residues within the oxyalkylene-carboxyalkylene polymers can, as a practical matter, be influenced to a considerable extent by a selection of the temperature at which the starting materials are reacted and the rate at which the reactants are fed to the reaction mixture, although theoretically an efficient distribution is possible at any temperature up to about 150 to 200° C. Generally, lower alkylene epoxides react more rapidly with hydroxyl groups than do the lactones. With increasing molecular weight, epoxides react more slowly, and approach the reaction rates of the lactones.

At lower temperatures, i.e., from about 10° C. to about 70° C., maximum intermixing of the lactone and epoxide residues is favored because then the rate at which the lactones react with the hydroxyl groups is slow enough to permit relatively accurate correlation therewith of the rate of addition of epoxide to the reaction mixture. Furthermore, the heat of the exothermic reactions can be removed more effectively at slower reaction rates, thus minimizing acceleration of the reaction rates due to increases in temperature. Thus, for example, if under the conditions of reaction five mols of lactone could be expected to add onto terminal hydroxyls in the course of five minutes, it would be relatively easy to obtain an oxyalkylene-carboxyalkylene polymer having chain segments alternately and repeatedly having an average of two epoxide residues and one lactone residue by mixing the lactone

with the hydroxyl-bearing compound, adding ten mols of epoxide in the course of five minutes and cooling the reaction mixture to keep the temperature, and therefore the reaction rates, relatively constant. This type of oxyalkylene-carboxylene polymer, in which the random distribution of the epoxide and lactone residues is relatively efficient, is characterized by water-insolubility and by not crystallizing even at temperatures as low as -30°C .

At higher temperatures, e.g., from about 70 to 100°C . or higher, the rates of reaction are considerably faster and the difficulties of removing the heat of the reactions for controlling the temperature of reaction are multiplied. As a result, such higher temperatures favor a less efficient distribution of the lactone and epoxide residues with the result that an oxyalkylene-carboxyalkylene polymer chain will contain a relatively large number of epoxide residues connected to one another in series and such series of epoxide residues are interrupted occasionally by series of lactone residues. Thus, for example, where the epoxide of lactone ratio is $2:1$, an oxyalkylene-carboxyalkylene polymer chain obtained at such a higher temperature and feed rate of epoxide may have an average of twenty or thirty epoxide residues connected in series to one another and such series of epoxide residues may be interrupted or terminated by fairly long series or blocks of polylactones having an average of ten or fifteen lactone residues. This type of oxyalkylene-carboxyalkylene polymer, in which the random distribution of epoxide and lactone residues is relatively inefficient, is characterized by water-solubility and a tendency to crystallize at temperatures of the order of 10 to 15°C .

It will be understood, therefore, that with this knowledge of the reactivity rates of epoxides relative to one another and relative to lactones, and the influence thereon of temperature conditions, suitable adjustments can readily be made to influence the reactions in desired directions and, therefore, the characteristics of oxyalkylene-carboxyalkylene polymers and resins prepared therefrom.

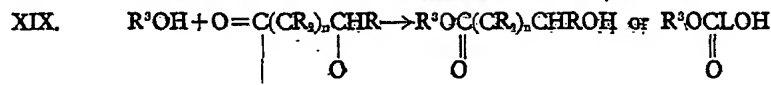
Higher temperatures within the operable range of about 10°C . to 150 or 200°C ., e.g.

above about 100°C ., are feasible provided the contact time is made correspondingly short so as to avoid dehydration side reactions, particularly when the catalyst is boron trifluoride. Lower temperatures, e.g., as low as 10°C ., are operable but require longer reaction times than are considered economically desirable. Generally, therefore, elevated temperatures up to about 100°C . are preferred and temperatures between about 50 and 70°C . are considered optimum for maximum production and control with minimum dehydration.

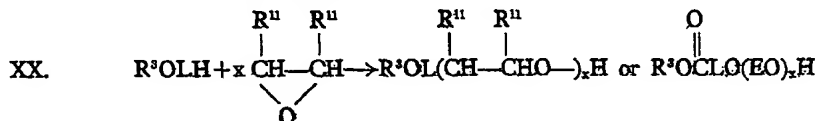
The reaction is preferably promoted by the presence of Lewis acids such as the trifluoride, tribromide and trichloride of boron, the bromides and chlorides of aluminum, tin and titanium, and the chlorides of antimony, beryllium, bismuth, cadmium, gallium, iron, uranium, zinc and zirconium. The preferred catalysts are boron trifluoride and its complexes with such organic compounds as ethers, alcohols, and polyols.

When the oxyalkylene-carboxyalkylene polymers are prepared in this manner, it is essential to use, as initiators for the polycondensation thereon of lactone and epoxide residues, difunctional focal compounds that do not contain nitrogen atoms for the reason that the Lewis acid catalysts employed in the reaction form inactive complexes with nitrogen atoms. When a flexible resin is the ultimate desideratum, it is advantageous to avoid using lactones that are substituted on the carbon atom adjoining the oxy group of the lactone, e.g. the epsilon carbon of an epsilon-caprolactone. Use of such lactones when a boron trifluoride complex is the catalyst apparently causes dehydration of the second hydroxyl group that is formed and then results in a branched-chain structure of high hydroxyl content that is desirable when the ultimate product is to be a rigid product.

The preparation of the oxyalkylene-carboxyalkylene polymers in the first stage of the method of the invention can also be accomplished in three steps to result in a relatively ordered distribution of oxy and carboxy groups. The first of these steps involves reacting the initial lactone or mixture of lactones with a molar excess of a monohydric alcohol as indicated in the equation:—



The reaction product of this step is then reacted with one or more 1,2-epoxides, as illustrated in the equation:—



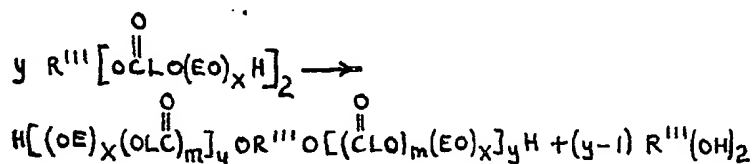
Finally, the resulting oxycarboxyalkylene monomer is reacted with an excess of difunctional focal compound acting as a chain

stopper, the reaction with a diol being illustrated by the equation:—



and the residual product self-polymerizes by interior ester groups and the elimination of interaction of its terminal hydroxyls with the excess difunctional compound:—

XXII.



It will be understood, of course, that an amino group on the chain stopper will result in a carbamido linkage between an oxyalkylene-carboxyalkylene chain and the chain stopper residue.

The alcohol used in the first step of this embodiment of the invention and symbolized in the equation as R^3OH is a primary or secondary monohydric alcohol having a lower boiling point than the difunctional chain stopper. Among those suitable for this purpose are aliphatic alcohols such as methanol, ethanol, propanol, isopropanol, 1-butanol, 2-butanol, tert.-butanol, 1-pentanol, 2-pentanol, tert.-amyl alcohol, 1-hexanol, 4-methyl-3-pentanol, 2-ethyl-1-butanol, 1-heptanol, 3-heptanol, 1-octanol, 2-ethyl-1-hexanol, 1-nonanol, 2,6-dimethyl-4-heptanol, 2,6,8-trimethyl-4-nonanol, 5-ethyl-2-nonanol, 7-ethyl-2-methyl-4-undecanol, 3,9-triethyl-6-decanol, and lauryl alcohol; aromatic alcohols such as benzyl alcohol and phenyl methyl carbinol; and cycloaliphatic alcohols such as cyclohexanol and trimethylcyclohexanol. Methyl and ethyl alcohols are preferred.

The lactones that are suitable as starting materials in the first step are the same as those previously identified by Formula V. The lactones having less than six carbon atoms in the ring, i.e., where n is less than four, can be used in accordance with this embodiment of the method even though homopolyesters thereof tend to revert to the monomer at elevated temperatures and therefore do not form stable products. They are suitable here because the addition of as little as one mol of a 1,2-epoxide per mol of lactone results in the preparation of linear oxyalkylene-carboxyalkylene polymers in which reversion to small rings is excluded. While it is true that with some of the lower molecular weight lactones somewhat less than 100%, i.e., about 80% and in some instances as low as 60%, conversion takes place, the oxyalkylene-carboxyalkylene polymers from these lower molecular weight lactones are

nevertheless entirely suitable for the purposes of the invention.

The first step in this more indirect manner of preparing the oxalkylene-carboxyalkylene polymers is preferably carried out at a temperature of the order of about 60 to 100° C. and in the presence of acidic ester interchange catalysts such as sulfuric, hydrochloric, phosphoric acids and boron trifluoride complexes such as trifluoride ethyl etherate. Basic and neutral ester interchange catalysts that also promote the reaction include such metals as lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, barium, strontium, zinc, aluminum, titanium, cobalt, germanium, tin, lead, antimony, arsenic and cerium, as well as the alkoxides thereof. Additional suitable catalysts are, by way of example, the carbonates of alkali- and alkaline earth metals, zinc borate, lead borate, zinc oxide, lead silicate, lead arsenate, litharge, lead carbonate, antimony trioxide, germanium dioxide, cerium trioxide, cobaltous acetate and aluminum isopropoxide. Catalyst concentrations between about 0.01 and about 0.5% by weight based on the total charge are suitable. The preferred range is from 0.05 to 0.2% by weight.

In order to obtain an optimum proportion of the hydroxy ester, it is important to utilize a considerable excess, e.g., five to twenty mols of alcohol per mol of lactone. Thus, for example, by working with a ten-fold excess of alcohol, 60 to 95% by weight of the lactone employed is converted to the hydroxy ester. The remainder consists either of unreacted lactone or of higher alcohol adducts, i.e., compounds in which two or more lactone residues are joined to an alcohol to form a higher molecular weight hydroxy ester. It is quite possible, however, to proceed with a somewhat smaller excess of alcohol and thereby obtain a hydroxy polyester adduct in which the average number of lactone residues added to the alcohol is in excess of one.

After the formation of the hydroxy ester

has been completed, the excess alcohol present in the reaction mixture must be removed. This is not conveniently accomplished by distillation at temperatures as high as 100° C. However, since the ester interchange catalysts used in this step to open the lactone ring also catalyze the reformation of alcohol and lactone, in some instances fairly rapidly at temperatures as low as 50° C., it is necessary to remove or to destroy the catalyst before removal of the excess alcohol. Acidic and basic catalysts such as sulfuric acid and sodium methoxide can easily be converted to inactive salts by neutralization, or they can readily be removed completely by means of ion exchange resins. If, however, the catalyst for the first step is destroyed by formation of an active salt, e.g., sodium sulfate, the hydroxy esters formed in the reaction of the first step must be distilled off because otherwise such salts would interfere with the catalytic process of the second step. Neutral ester interchange catalysts, while plentiful and operable, are difficult to remove or to destroy and are therefore not preferred.

In the second step of the alternative method for preparing the oxyalkylene-carboxyalkylene polymers, the hydroxy esters formed in the first step are reacted with 1,2-epoxides in the presence of a catalyst to form lengthened hydroxy esters containing ether groups. The epoxides that are suitable in this step are those that have already been described as corresponding to Formula V. Mixtures of these epoxides are also suitable and in some instances preferred for desirably altering the structure of the oxyalkylene-carboxyalkylene polymers. Ethylene and propylene oxide and mixtures thereof are preferred because of their low cost and ease of reaction.

The catalysts that are most suitable for the second step are the Lewis acids named earlier, particularly boron trifluoride and the complexes thereof with organic compounds as well as aluminum trichloride, zinc chloride and tin chloride. Bases such as tertiary organic amines, sodium and potassium methoxides and hydroxides may also be employed although they are considered not as suitable because they require relatively high reaction temperatures of the order of 90 to 150° C. and high catalyst concentrations of the order of 0.2 to 2% by weight in order to be effective. Thus, while these other catalysts are operable, they are not preferred because of the high temperatures and catalyst concentrations that are necessary and which tend to promote reversion of the hydroxy esters to the initial lactones and alcohols. Boron trifluoride complexes such as the ethyl etherate are preferred.

The operable range of reaction temperatures for the second step of this alternative method is from below about 10° C. to about 150° C. At the lower temperatures in this

range the reaction proceeds slowly, while at higher temperatures there is danger of ring closure of the hydroxy ester with formation of lactone and alcohol. The preferred temperature range is from 45 to 100° C. since it allows rapid reaction rates with a minimum of reversion to the lactone.

Any unreacted lactone from the first step that remains at the beginning of the second step will take part in the reaction with the 1,2-epoxide when a Lewis acid catalyst is employed. The amount of such lactone reacting in the second step depends upon the duration and the temperature of the reaction, the catalyst concentration as well as on the structure of the lactone and the epoxide used.

The oxy-carboxyalkylene monomers obtained in accordance with the second step are polymerized in the third step with the aid of a difunctional focal compound acting as a chain stopper to form linear oxyalkylene-carboxyalkylene polymers of any desired preselected molecular weight. Difunctional focal compounds acting as chain stoppers in this alternative method of preparation yield linear polymers, as they do when used as initiators in the more direct process described earlier.

The difunctional focal compounds that are suitable as chain stoppers in the third step of this alternative method are generally the diols, diamines and amino alcohols represented by Formula VII.

It is important, from the point of view of exercising control over the molecular weight of the oxyalkylene-carboxyalkylene polymers, to use a considerable excess, preferably about five- to ten-fold the amount of stoichiometrically required, of difunctional focal compound in the third step and that it be one having a higher boiling point than the alcohol used in the first step. This excess and higher boiling point is required in order to insure a substantial displacement of the monofunctional alcohol from the intermediate product of the second step. In instances in which the focal compound itself is difficult to remove, e.g., when a considerably higher boiling diol is employed, the preferred procedure is to use a stoichiometric amount thereof in conjunction with a substantial excess of another diol that is relatively easy to remove. Thus, for example, where the alcohol used in the first step is methanol and the desired chain stopper is triethylene glycol, it is possible by this procedure to remove substantially completely all of the methanol with a considerable excess of added ethylene glycol and preferentially to retain in the polymer the stoichiometric amount of triethylene glycol initially used rather than the ethylene glycol.

The third step in the alternative method of preparing the oxyalkylene-carboxyalkylene polymers in the first stage is preferably, but not necessarily,

carried out with the use of a catalyst such as a basic or neutral ester interchange catalyst to accelerate the reaction. Among the catalysts that are suitable for this purpose are such metals as lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, barium, strontium, zinc, aluminum, titanium, cobalt, germanium, tin, lead, antimony, arsenic and cerium, as well as the alkoxides thereof. Additional suitable catalysts are, by way of example, zinc borate, lead borate, zinc oxide, lead silicate, lead arsenate, litharge, lead carbonate, antimony trioxide, germanium dioxide, cerium trioxide, magnesium acetate, cobaltous acetate, manganese acetate, lead acetate, lead 2-ethylhexoate, lead salicylate and lead benzoate. Catalyst concentrations between about 0.001 and 1.0% by weight, based on the weight of the starting monomer, are suitable. The preferred range is from 0.01 to 0.5% by weight based on the weight of the starting monomer. The catalyst has also the function of destroying the boron trifluoride complex left in the reaction mixture of the preceding step, which, if not inactivated, may cause side reactions such as dehydration.

The catalysts that are particularly effective, and therefore preferred, in polymerizing the monomers are the organic tin compounds described in copending Application No. 12159/57 (Serial No. 859,639) the organic titanium compounds described in copending Application No. 12162/57 (Serial 859,642) and the titanium chelates and acylates described in copending Application No. 12164/57 (Serial No. 859,644).

The third step is carried out within the temperature range of 120 to 250° C., most effectively between about 150 and 200° C. It is preferably carried out in two phases, the first at a temperature of about 120 to 170° C. and the later phase, for further polymerization, at 150 to 250° C. At temperatures below 150° C. the reaction rate is relatively slow whereas at temperatures above 200° C. there is a danger that thermal degradation of the reactants and products may begin to occur. It is desirable, therefore, to carry out the final phase of the third step under a vacuum and to exclude air from the reactants by blowing an inert gas such as nitrogen through the reaction mixture.

The average molecular weight and reactivity of the mixture of oxyalkylene-carboxyalkylene polymers with an isocyanate can readily be determined by analysis for hydroxyl and carboxyl content. The acid or carboxyl number (mg. of KOH per gram of oxyalkylene-carboxyalkylene polymer using phenolphthalein as an indicator) is a measure of the number of terminal carboxyl groups. The hydroxyl number, which is a measure of the number of terminal hydroxyl groups and is

defined in terms of mg. of KOH per gram of oxyalkylene-carboxyalkylene polymer, is determined by adding pyridine and acetic anhydride to the oxyalkylene-carboxyalkylene polymer and titrating the acetic acid formed with KOH. The sum of the acid or carboxyl number and the hydroxyl number, referred to as the reactive number, is an indication of the average number of terminal groups present in the oxyalkylene-carboxyalkylene polymer and therefore is in turn an indication of the degree of polymerization. A mixture of oxyalkylene-carboxyalkylene polymers containing long chain molecules will have a relatively low reactive number while oxyalkylene-carboxyalkylene polymers containing short chains will possess relatively higher reactive numbers. Molecular weight can readily be calculated from the hydroxyl and carboxyl number by the formula:—

$$\text{XXIII. M.W.} = \frac{2000 \times 56.1}{\text{OH No.} + \text{COOH No.}}$$

It will become apparent from the foregoing that regardless of how the linear oxyalkylene-carboxyalkylene polymers are made, i.e. whether they are block oxyalkylene-carboxyalkylene polymers or whether the distribution of carboxy and oxy groups in the chain is random or ordered, they can be prepared to best suit the particular type and requirements of the polyurethane resin ultimately desired. The molecular weight of block oxyalkylene-carboxyalkylene polymers can be controlled accurately by a preselected proportion of the difunctional focal compounds reacted with the lactone and the epoxide or retained in the oxyalkylene-carboxyalkylene polymers. The smaller the amount of initial glycol or difunctional focal compound is relative to the lactone or to the lactone and the epoxide, as the case may be, the higher will be the molecular weight of the oxyalkylene-carboxyalkylene polymer. The relative proportions of oxy and carboxy groups can readily be controlled by the proportions of lactone to glycol or epoxide. Oxyalkylene-carboxyalkylene polymers prepared primarily from epsilon-caprolactone and ethylene oxide to have molecular weights of the order of about 1800 to 2800 and in which the oxy groups outnumber the carboxy groups by ratios of the order of about 3.2:1 to 6.5:1 are from slightly to completely water-soluble whereas those in which the ratio of oxy to carboxy groups is of the order of about 0.5:1 to about 3.2:1 are water-insoluble liquids. The extent to which the occurrence of oxy and carboxy groups is random or ordered can be influenced by the availability of the components for reaction in the course of preparation. This in turn can be controlled by selections of reaction temperature and rate of feed of epoxide to the reactants. Side chains can be introduced by the use of substituted lactones,

substituted glycols or epoxides, or both. If desired, the oxyalkylene-carboxyalkylene polymers can also be given a branched structure by employing polyols having a functionality higher than two in the preparation of block oxyalkylene-carboxyalkylene polymers and by the use of diepoxides or polyfunctional focal compounds having more than two reactive hydrogens, or both, in the preparation of oxyalkylene-carboxyalkylene polymers with random or ordered distribution of oxy and carboxy groups.

We prefer to select the lactones and the epoxides and difunctional focal compound, and their relative proportions, so as to produce oxyalkylene-carboxyalkylene polymers having molecular weights in the range of about 400 to as high as about 10000 and preferably between about 1800 and 2800.

When oxyalkylene-carboxyalkylene polymers having molecular weights as low as about 400 are employed in the preparation of polyurethane resins by reaction with isocyanates, the resins formed are relatively rigid. On the other hand, oxyalkylene-carboxyalkylene polymers having molecular weights in the upper end of the range, e.g., around 5000 to 7000, result in the formation of polyurethane resins of very high elasticity. Generally speaking, polyurethane resins prepared from block-type oxyalkylene-carboxyalkylene polymers of a given molecular weight tend to form polyurethane resins having somewhat higher tensile strength than those formed from random or ordered type of oxyalkylene-carboxyalkylene polymers of equal molecular weight.

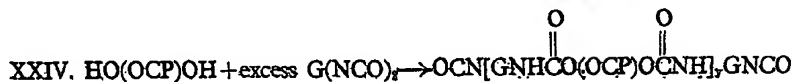
As a further guide to the selection of initial reactants and their relative proportions for the formation of oxyalkylene-carboxyalkylene polymers and their eventual conversion into polyurethane resins, it is well to bear in mind also that oxyalkylene-carboxyalkylene polymers derived from unsubstituted lactones generally tend to have superior tensile strength and some tendency to crystallize, whereas those made from oxyalkylene-carboxyalkylene polymers derived from substituted lactones, at least in part, show no tendency to crystallize and tend to form elastomers having optimum non-hardening properties.

Inasmuch as the block-type oxyalkylene-carboxyalkylene polymers tend to impart maximum tensile strength to polyurethane resins formed from them and oxyalkylene-carboxyalkylene polymers having random or ordered distribution of oxy and carboxy groups favor good low temperature properties, it will become apparent that optimum tensile strength is obtainable by use of block-type oxyalkylene-carboxyalkylene polymers prepared from unsubstituted lactones as the only lactones and that optimum low temperature properties are obtainable by use of oxyalkylene-carboxyalkylene polymers of the random or ordered type prepared, at least in part, from substituted lactones.

It is to be understood of course that the term "oxyalkylene-carboxyalkylene polymers", as used herein, is intended to include not only the oxyalkylene-carboxyalkylene polymers prepared by reaction of a single lactone with a single epoxide and difunctional focal compound, but also those involving two or more lactones, epoxides or focal compounds. Furthermore, it is to be understood that it is within the scope of the invention to react diisocyanates with not only one particular mixture of oxyalkylene-carboxyalkylene polymers but also with blends of different oxyalkylene-carboxyalkylene polymer mixtures prepared as herein described as well as with blends of one or more of the oxyalkylene-carboxyalkylene polymers with polyesters heretofore described, e.g., the lactone polyesters described in co-pending Application No. 12162/57 (Serial No. 659,642) or high molecular weight polyalkylene ethers or polyesters such as those prepared by condensation of a glycol with a dicarboxylic acid.

SECOND STAGE (LINEAR EXTENSION)

We have found it advantageous to extend the oxyalkylene-carboxyalkylene polymers by reacting, after careful removal of any traces of moisture, their terminal hydroxyl groups with an excess of diisocyanate, as represented by the equation:—



in which HO(OCF)OH is an abbreviated representation for the oxyalkylene-carboxyalkylene polymers with their characteristic terminal hydroxyl groups and chains of divalent alkylene links connected by oxy and carboxy groups, G stands for a member selected from the group consisting of divalent aliphatic, aromatic cycloaliphatic radicals and γ is an average of at least one and preferably about two or more.

It will be noted from Equation XXIV that the use of an excess of diisocyanate provides

an efficient means of control over the degree of linear extension of the oxyalkylene-carboxyalkylene polymers. If the proportions of oxyalkylene-carboxyalkylene polymer and diisocyanate are chosen so that the number of reactive terminal hydroxyl groups on the oxyalkylene-carboxyalkylene polymers are equal to the number of reactive isocyanate groups on the diisocyanate, extremely long, high molecular weight chains would be formed with alternately recurring oxyalkylene-carboxyalkylene chains and diisocyanate residues,

y in that instance possibly being a very high number. The resulting resin would have a sharp melting point, retain its original solubility properties, and be capable of being drawn into filaments. By utilizing an optimum excess of about 30 to 60% by weight diisocyanate however, close control is maintained over the length of the isocyanate-modified oxyalkylene-carboxyalkylene polymer in that the molecules formed predominantly comprise two to three oxyalkylene-carboxyalkylene chains conjugated with three to four, respectively, diisocyanate residues, y being an average of 3.33 with a diisocyanate excess of 30% and an average of 1.66 with a diisocyanate excess of 60% by weight. Diisocyanate-modified oxyalkylene-carboxyalkylene polymers within this range have the most desirable characteristics for the production, at a later stage, of a rubbery polymer which softens gradually over a wide range of temperatures and is not subject to cold drawing. A greater excess, up to several hundred percent, of diisocyanate is desirable if the desideratum is a more rigid type of polyurethane product.

The reaction of the oxyalkylene-carboxyalkylene polymers with the diisocyanate can take place at temperatures varying from room temperature to above 300° C. The preferred temperature is in the range of about 100 to 150° C., the upper limit of the reaction temperature being selected on the basis of the thermal stability of the reaction products and of the diisocyanates, and the lower limit being determined by the lowest economical rate of reaction without a catalyst. At temperatures under this range, the reaction is entirely feasible if a catalyst is employed. Without a catalyst it is too slow to be practicable, especially at temperatures below about 75° C. At temperatures above 200° C., and particularly above about 300° C., there is danger of destructive decomposition of the reactants and reaction product.

The time of reaction may vary from several minutes to as much as a day depending upon the reaction temperature and the identity of the particular oxyalkylene-carboxyalkylene polymer and diisocyanate as well as upon the absence or presence of accelerator or retarder and the identity thereof. Most desirably, conditions are adjusted so as to provide a controllable reaction that is completed in about ten to sixty minutes.

If desired, the reaction may be accelerated by employing catalysts such as inorganic bases and particularly tertiary organic bases such as tertiary amines and phosphines. Among the latter are N,N'-dimethylaniline, N,N'-dimethylhexahydroaniline, N,N'-dimethylpiperazine, N-methylmorpholine, triethylamine, N,N'-dimethylbenzylamine, triethylamine, trialkyl phosphines, dialkylphenyl phosphines and alkylidiphenyl phosphines. Catalyst concentrations may be varied

considerably. Concentrations between about .001 and .5% based on the weight of the total ingredients, have been found sufficient.

Among the retarders suitable for the oxyalkylene-carboxyalkylene polymer-diisocyanate reaction are acids such as hydrochloric acid, sulfuric acid, phosphoric acid, boric acid, and organic acids; acyl halides such as acetyl chloride and acetyl bromide; sulfonyl halides such as para-toluene-sulfonyl-chloride; inorganic acid halides such as phosphorous tribromide, phosphorous trichloride, phosphorous oxychloride, sulfuryl chloride, and thionyl chloride; and sulfurdioxide or acidic sulfones. The addition of a retarder is desirable in some instances not only in order to slow down, as the name implies, the rate of reaction between terminal hydroxyl and isocyanate groups, but also for inhibiting reaction between the isocyanate groups and the urethane groups formed in the second stage.

If the starting oxyalkylene-carboxyalkylene polymers from the first stage contain alkaline reacting materials, they should be neutralized or acidified slightly by addition of acids or acid chlorides. For instance, polyethylene oxides are prepared by catalyzing the ethylene oxide polymerization with sodium or potassium hydroxide or other basic catalysts. If these polyethylene oxides are reacted with lactone, the resulting block-type oxyalkylene-carboxyalkylene polymers contain some sodium or potassium carboxylate end groups which are efficient catalysts for the isocyanate reaction in stage two. In order to prevent almost instantaneous or premature cross-linking in stage two (a procedure which yields inferior elastomers), the oxyalkylene-carboxyalkylene polymers should be neutralized or slightly acidified.

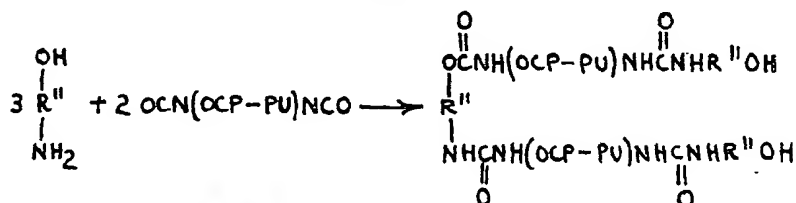
The chain lengthening reaction of the oxyalkylene-carboxyalkylene polymers with the diisocyanate may be carried out with a wide variety of aliphatic, cycloaliphatic or aromatic diisocyanates, the aromatic diisocyanates being most suitable because of their greater reactivity. Among the various diisocyanates useful in this reaction are m- and p-phenylene diisocyanates, 2,4- and 2,6- tolylene diisocyanates, 2,3,5,6-tetramethyl-para-phenylene diisocyanate, m-xylylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, p,p'-bibenzyl diisocyanate, p,p'-diphenylmethane diisocyanate, 4,4'-methylene bis ortho tolyl isocyanate, 1,5-naphthalene diisocyanate, fluorene diisocyanates, pyrene diisocyanates and chrysene diisocyanates. The table in the publication of Sieffen (Annalen, 562, pages 122-135 (1949)) lists numerous other diisocyanates which are useful for performing this reaction.

THIRD STAGE (GUM STOCK PREPARATION)

In order to further extend the oxyalkylene-carboxyalkylene polymer-polyurethane diisocyanates obtained in the second stage and also to bring about a cross-linking of the molecules, the oxyalkylene-carboxyalkylene polymer-polyurethane is reacted with a difunctional reactant which is a diol, a diamine or an amino alcohol. Such a further chain lengthening reaction to form a gum stock is

illustrated, by way of example, in Equation XXV below. In this illustrative example, two mols oxyalkylene-carboxyalkylene polymer-polyurethane diisocyanate, abbreviated for purposes of clarity as OCN(OCP-PU)NCO to indicate the reactive terminal isocyanate groups obtained by using an excess of diisocyanate in stage two, react with three mols of an amino alcohol to show the reactions of hydroxyl and amino groups of a difunctional reactant with the isocyanate groups.

XXV.



It will be evident from Reaction XXV that the hydroxyl group of a difunctional reactant in this stage reacts with a terminal isocyanate group to form a urethane group —OOCNH— and that the amino group of a difunctional reactant does so by forming a ureylene group —HNCONH—. There is reason to believe that, simultaneously with Reaction XXV, the reaction products of Reaction XXV and free diisocyanates react to effect a cross-linking. These reactions can take place in many ways. Thus, for example, a terminal isocyanate group can react with a reactive hydrogen or (a) an amide group of a stage two product or a stage three product prepared initially with the polyalkylene ether having one or two amino groups to form an acyl urea cross link, (b) a urethane group of a stage two product or a stage three product (Equation XXV) to form an allophanic ester cross link, and (c) a ureylene group of a stage three product prepared with an amino group-containing reactant to form a biuret cross link. Some of these reactions may also take place, albeit at a much reduced rate, before the addition of the difunctional reactant in the third stage, because of the formation of a number of urethane groups in the second stage and their ability to enter into slow cross linking reaction with terminal isocyanate groups.

The difunctional reactants that are useful in this stage are diols, amino alcohols or diamines. It is inadvisable, however, where high tensile strength of the final product is desirable, to use those of higher molecular weight than, for example, polyoxyalkylene compounds of the formulae $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ and $\text{HO}[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]_n\text{H}$ where n is greater than about six. Among the difunctional reactants found to be particularly suitable alone or in admixture with one another in this stage are ethylene glycol, trimethylene

glycol, 1,4-butylenediol, 1,4-butenediol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, decamethylene glycol, quinitol, ethanolamine, 3-aminopropanol, 4-aminobutanol, 5-aminopentanol, 6-amino-hexanol, *p*-aminobenzyl alcohol, *m*-amino- α -methylbenzyl alcohol, *p*-aminophenylethyl alcohol, ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, decamethylenediamine, *m*-phenylenediamine, 2,4-tolylenediamine, *p*-phenylenediamine, 4,4'-biphenylenediamine, 3,3'-dichloro-4,4'-biphenylenediamine, 3,3'-dimethyl-4,4'-biphenylenediamine, 3,3'-dimethoxy-4,4'-biphenylenediamine, *p,p'*-bibenzylidiamine, *p,p'*-diphenylmethanediamine, 2,5- and 2,7-fluorenylenediamines, 3,8- and 3,10-pyrenediamines, piperazine, various methyl-, and polymethylpiperazines. Difunctional reactants of this type are preferred in this stage of the process for the reason that they act as chain extenders without forming carbon dioxide bubbles in the mass.

While reaction XXIV is shown for illustrative purposes only, as involving three mols of a difunctional reactant and two mols of a oxyalkylene-carboxyalkylene polymer-polyurethane diisocyanate, i.e., a 50% excess of a difunctional reactant, the amount of difunctional employed for optimum results is within the range of 1 to 20% excess. The use of more than 20% excess results in a system that is generally more rigid than desirable for the production of elastomeric materials and the use of an equivalent or less than equivalent amount of difunctional results in a completely cross-linked system which ceases to be a gum stock. It is to be understood, therefore, that while a 1 to 20% excess of difunctional reactant is recommended for the third stage, departures from this amount in order to obtain more rigid or more com-

reactant, the number of reactive isocyanate groups in this instance being less than the number of hydroxyl and amino groups available for reaction on the oxyalkylene-carboxyalkylene polymers and polyfunctional reactant. This is in effect a combination of the second and third stages for the preparation of the non-hardening gum stock and is followed by addition and reaction with an excess of additional isocyanate, preferably about 3 to 7%, in order to effect a cure. This embodiment, as well as the embodiment described in detail as most illustrative of the mechanism of the reactions involved, is desirable when it is desired to form a non-hardening gum stock than can be cured at a future date.

A considerable number of modifying agents may be added to the polyurethane resin at any stage of its production after the formation of the oxyalkylene-carboxyalkylene polymer. These materials include fillers such as carbon blacks, various clays, zinc oxide, titanium dioxide, and the like; various dyes; plasticizers such as polyesters which do not contain any reactive end-groups, stearic and other fatty acids, organic esters of stearic and other fatty acids, metal salts of fatty acids, dioctyl phthalate, tetrabutylthiodisuccinate, and the like. It is also possible to include releasing agents such as mold release agents that are sometimes very helpful in the processing of the resin to about 130° C. After the mixture had cooled to 120° C., 2.5 grams ethanolamine were added and the materials were stirred until an elastomeric gum stock resulted. This was milled into a thin sheet on a rubber mill.

EXAMPLE 1

912 grams (8 mols) epsilon-caprolactone and 2560 grams (80 mols) methanol were heated to 65 to 67° C. for twenty hours in the presence of 0.456 gram concentrated sulfuric acid (96%) as catalyst. The acid catalyst was then neutralized by addition of 0.505 gram sodium methylate and distilled *in vacuo*. 971 grams of methyl 6-hydroxycaproate were obtained. It had a boiling point of 99° C. at a pressure of 4 mm. Hg. and a refractive index n_D^{20} of 1.4349 to 1.4352.

877.2 grams (5 mols) of the methyl 6-hydroxycaproate thus obtained were heated to 60° C. with 2.80 grams boron trifluoride ethyl etherate (47% BF_3) and then 528 grams (12 mols) ethylene oxide were added over a period of three hours at a temperature of 60 to 70° C. The resulting ethylene oxide adduct was a colorless liquid having a refractive index n_D^{20} of 1.4460.

550 grams of the ethylene oxide adduct, 31 grams (0.5 mol) ethylene glycol and 1.1 gram tetraisopropyl titanate were heated at 170° C. for twenty hours. 87.5 ml. of methanol were recovered. The reactants were then subjected to a vacuum of 10 mm. Hg. for 3.5 hours at 170° C., 15 grams of ethylene glycol being recovered. The resulting mixture of oxyalkylene-carboxyalkylene polymers was a light yellow viscous liquid having a hydroxyl number of 51.1, a carboxyl number of 1.0 and a calculated average molecular weight of 2120.

300 grams of the oxyalkylene-carboxyalkylene polymers were heated to 120° C. with 56.1 grams (0.212 mol) 3,3-dimethyl-4,4'-diphenylene diisocyanate. The reaction temperature rose to 130° C. After the reactants had cooled to 120° C., 5.2 grams ethanolamine were added and the reactants were stirred vigorously until an elastomeric gum stock resulted. This was milled into a thin sheet on a rubber mill.

5% by weight of 3,3'-dimethyl-4,4'-diphenylene diisocyanate was admixed with a portion of the gum stock on a cold rubber mill. The material was then molded into a disc of 0.07" thickness by heating under pressure for fifteen minutes at 160° C. The cured elastomer exhibited the following physical properties:—

Tensile strength, Kg./sq.cm.	- - -	135
Elongation at break, %	- - -	780
Load at 300% elongation, Kg./sq.cm.	- - -	39
Brittle temperature, °C.	- - -	-64
Hardness—Shore "A"	- - -	54

EXAMPLE 2

550 grams of the ethylene oxide adduct of methyl 6-hydroxycaproate, prepared as described in Example 1, and 31 grams (0.5 mol) ethylene glycol were heated at 170° C. for twenty hours in the presence of 0.55 gram dibutyltin oxide and 0.5 gram tetraisopropyl titanate as catalysts. 80 ml. of methanol were recovered during this reaction. The reactants were then subjected to a vacuum of 10 mm. Hg. for three hours during which time 15 grams of ethylene glycol were recovered. The resulting mixture of oxyalkylene-carboxyalkylene polymers was a colorless viscous liquid having a hydroxyl number of 59.2, a carboxyl number of 1.3 and a calculated average molecular weight of 1820.

150 grams of the oxyalkylene-carboxyalkylene polymers thus obtained were heated to 120° C. and 31.3 grams (0.1185 mol) 3,3'-dimethyl-4,4'-diphenylene diisocyanate were added, whereupon the reaction temperature rose to 135° C. After the mixture had cooled at 120° C., 2.9 grams ethanolamine were added and the materials were stirred until an elastomeric gum stock resulted. This was milled into a thin sheet on a rubber mill.

7% by weight of 3,3'-dimethyl-4,4'-diphenylene diisocyanate was added to a portion of this gum stock on a cold rubber mill. The mixture was molded into a disc of 0.07" thickness by heating under pressure for fifteen minutes at 160° C. The cured elastomer possessed the following physical properties:—

Tensile strength, Kg./sq.cm. - -	138
Elongation at break, % - - -	735
Load at 300% elongation, Kg./sq.cm. - - -	127
5 Brittle temperature, °C. - - -	-52
Hardness—Shore "A" - - -	65

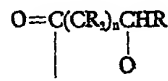
EXAMPLE 3

1406 grams of epsilon-caprolactone, 79.5 grams of ethylene glycol and 3.3 grams of borontrifluoride ethyl etherate (47% BF₃) were heated to 60° C. 1406 grams of ethylene oxide were then fed to the reaction mixture over a period of 5.4 hours. On application of a vacuum of 4 mm. Hg., 81 grams of dioxane were removed. The remaining mixture of oxyalkylene-carboxyalkylene polymers had a hydroxyl number of 52.5 and a carboxyl number of 1.3.

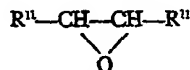
204 grams of the above oxyalkylene-carboxyalkylene polymers and 11.0 grams of 4,4'-methylenedianiline were heated to 120° C. A mixture of 65% 2,4- and 35% 2,6-tolylene diisocyanate (33.0 grams) was then added and the reactants were stirred for forty-five minutes. After further curing at room temperature for twenty-four hours, a tough elastomeric product resulted.

WHAT WE CLAIM IS:—

1. A method of preparing a gum stock which comprises forming a mixture of oxyalkylene-carboxyalkylene polymers by reacting a diphenol, a diol, a diamine, an amino alcohol, a dimercaptan, a mercapto alcohol, water or hydrogen sulphide, a lactone of the general formula:—



in which n is an integer having a value of at least 2, all the Rs are hydrogen when n is 2, at least 6 Rs are hydrogen when n is more than 2 and the remaining Rs are hydrogen or alkyl, cycloalkyl, alkoxy or single ring aromatic hydrocarbon radicals or an hydroxy ester of said lactone and a primary or secondary alcohol having a boiling point lower than that of said diol, diamine, amino alcohol, dimercaptan, mercapto alcohol, water, hydrogen sulphide or diphenol, and a 1, 2 epoxide of the general formula:—



50 in which R¹ is hydrogen or an alkyl, chloroalkyl, hydroxyalkyl, vinyl or phenyl radical or in which the two R¹'s taken together complete a closed hydrocarbon ring; reacting said reaction mixture with a molar excess as hereinbefore defined of an organic diisocyanate to form isocyanate-extended oxyalkylene-carboxyalkyl-

ene polymers and converting said polymers to a non-hardening gum stock by reaction with a diol, a diamine, or an amino alcohol.

2. A method as claimed in Claim 1 in which n is at least 4 and at least (n+2) Rs are hydrogen.

3. A method as claimed in Claim 1 or 2 in which the hydroxy ester of the lactone is reacted with the 1,2-epoxide and the reaction product is then with an excess of the diphenyl, diol, diamine, amino alcohol, dimercaptan, mercapto alcohol, water or hydrogen sulphide.

4. A method as claimed in Claim 1 or 2, in which the lactone, the 1,2-epoxide, and the diphenyl, diol, diamine, amino alcohol, dimercaptan, mercapto alcohol, water or hydrogen sulphide are reacted at a temperature in the range from 10° to 70° C., in the presence of Lewis acids as catalysts.

5. A method as claimed in any of Claims 1 to 4 in which the mixture of lactone and 1,2-epoxide is reacted with a thirty to sixty percent molar excess of an organic diisocyanate.

6. A method as claimed in any of Claims 1 to 5 in which the isocyanate-extended oxyalkylene-carboxyalkylene polymers are reacted with 1 to 20 percent molar excess of the diol, diamine or amino alcohol.

7. A method as claimed in any of Claims 1 to 6 in which the gum stock is cured by reaction with an organic polyisocyanate.

8. A method as claimed in Claim 7 in which from 3 to 7 weight percent of the organic polyisocyanate is used to cure the gum stock.

9. The method as claimed in any of Claims 1 to 8 in which the mixture of lactone and 1,2-epoxide is reacted with the organic diisocyanate at a temperature between 50° and 200° C. and the resulting product is reacted with the diol, diamine or amino alcohol at a temperature between 50° and 200° C.

10. The method as claimed in Claim 9 in which the temperatures are between 100° and 150° C.

11. The method as claimed in any of Claims 1 to 5 in which the amount of diisocyanate is such that the number of reactive isocyanate groups in the reaction mixture is less than the number of hydroxyl and amino groups in the reaction mixture.

12. A method as claimed in any of Claims 1 to 4 in which the amount of organic diisocyanate is sufficient to provide an excess of 10 to 100% of isocyanate groups over the reactive hydrogen atoms provided by the diol, diamine or amino alcohol.

13. Non-hardening gum stocks prepared by the processes claimed in Claims 1 to 6 or 11 or 12.

14. Cured gum stocks prepared by the processes claimed in Claims 7 to 12.

15. A method of preparing a gun stock substantially as described herein with reference to and as illustrated in the foregoing examples.

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